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(54) **Low volatility solvent-based precursors for nanoporous aerogels**

Wenig flüchtiges Lösungsmittel enthaltender Vorläufer für nanoporöses Aerogel

Précurseurs pour aérogels nanoporeuse à base de solvant peu volatile

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mers or oligomers can be added to this molecule in a somewhat random fashion to create a highly branched polymeric molecule from literally thousands of monomers. An oligomerized metal alkoxide, as defined herein, comprises molecules formed from at least two alkoxide monomers, but does not comprise a gel.

[0007] Sol-gel reactions form the basis for *xerogel* and *aerogel* film deposition. In a typical thin film xerogel process, an ungelled precursor sol may be applied (e.g., spray coated, dip-coated, or spin-coated) to a substrate to form a thin film on the order of several microns or less in thickness, gelled, and dried to form a dense film. The precursor sol often comprises a stock solution and a solvent, and possibly also a gelation catalyst that modifies the pH of the precursor sol in order to speed gelation. During and after coating, the volatile components in the sol thin film are usually allowed to rapidly evaporate. Thus, the deposition, gelation, and drying phases may take place simultaneously (at least to some degree) as the film collapses rapidly to a dense film. In contrast, an aerogel process differs from a xerogel process largely by avoiding pore collapse during drying of the wet gel. Some methods for avoiding pore collapse include wet gel treatment with condensation-inhibiting modifying agents (as described in Gnade '802) and supercritical pore fluid extraction.

SUMMARY OF THE INVENTION

[0008] The present invention is directed to a metal-based aerogel precursor sol, comprising a metal-based aerogel precursor sol, comprising an aerogel precursor reactant selected from the group consisting of metal alkoxides, at least partially hydrolyzed metal alkoxides, particulate metal oxides, and combinations thereof, and a polyol as a first solvent, the polyol being selected from the group of glycerol, ethylene glycol, 1,4-butylene glycol, 1,5-pentanediol, 1,2,4-butanetriol, 1,2,3-butanetriol, 2-methyl-propanetriol, 2-(hydroxymethyl)-1,3-propanediol, 1,4,1,4-butanediol, 2-methyl-1,3-propanediol, and combinations thereof, wherein the molar ratio of said first solvent molecules to the metal atoms in said reactant is at least 1:16.

[0009] The invention further pertains to a non-supercritical method of forming a nonoporous aerogel, said method comprising the steps:

providing an aerogel precursor sol as defined in any one of claims 1 to 25, said sol being dispersed in said first solvent and a second solvent,

evaporating substantially all of said second solvent while preventing substantial evaporation of said first solvent, and allowing the sol to create a gel, wherein the gel comprises a porous solid and a pore fluid;

continuing to prevent substantial evaporation of said first solvent from said sol until a drying step,

wherein said drying step comprises forming a dry aerogel by removing the pore fluid in a non-supercritical drying atmosphere without substantial collapse of the porous solid;

whereby the skeletal density of the dry aerogel is determined approximately by the volume ratio of said aerogel precursor reactant to said first solvent in said aerogel precursor sol.

[0010] Between aerogels and xerogels, aerogels are the preferable of the two dried gel materials for semiconductor thin film nanoporous dielectric applications. Typical thin film xerogel methods produce films having limited porosity (up to 60% with large pore sizes, but generally substantially less than 50% with pore sizes useful in submicron semiconductor fabrication). While some prior art xerogels have porosities greater than 50%; these prior art xerogels had substantially larger pore sizes (typically above 100 nm). These large pore size gels have significantly less mechanical strength. Additionally, their large size makes them unsuitable for filling small (typically less than 1 μm , and potentially less than 100 nm) patterned gaps on a microcircuit and limits their optical film uses to only the longer wavelengths. A nanoporous aerogel thin film, on the other hand, may be formed with almost any desired porosity coupled with a very fine pore size. Generally, as used herein, nanoporous materials have average pore sizes less than about 25 nm across, but preferably less than 20 nm (and more preferably less than 10 nanometers and still more preferably less than 5 nanometers). In many formulations using this method, the typical nanoporous materials for semiconductor applications may have average pore sizes at least 1 nm across, but more often at least 3 nm. The nanoporous inorganic dielectrics include the nanoporous metal oxides, particularly nanoporous silica.

[0011] In many nanoporous thin film applications, such as aerogels and xerogels used as optical films or in microelectronics, the precise control of film thickness and aerogel density are desirable. Several important properties of the film are related to the aerogel density, including mechanical strength, pore size and dielectric constant. It has now been found that both aerogel density and film thickness are related to the viscosity of the sol at the time it is applied to a substrate. This presents a problem which was heretofore unrecognized. This problem is that with conventional precursor

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should be held fairly constant for a period of time in order for aging to occur. If pore fluid evaporates from the film before aging has strengthened the network, the film will tend to densify in xerogel fashion. On the other hand, if excess pore fluid condenses from the atmosphere onto the thin film before the network has been strengthened, this may locally disrupt the aging process and cause film defects.

[0021] Thus, we now know that some method of pore fluid evaporation rate control during aging is beneficial to aerogel thin film fabrication. In principle, evaporation rate control during aging can be accomplished by actively controlling the pore fluid vapor concentration above the wafer. However, the total amount of pore fluid contained in, for instance, a 1 mm thick 70% porous wet gel deposited on a 150 mm wafer is only about 0.012 mL, an amount that would easily fit in a single 3 mm diameter drop of fluid. Typical thin films used for nanoporous dielectrics on semiconductor wafers are approximately 1000 times thinner. Thus, actively controlling the pore fluid vapor concentration (by adding or removing solvent to the atmosphere) to allow no more than, e.g., 1%, or less, pore fluid evaporation during aging presents a difficult proposition; the surface area of the thin film is high and the allowable tolerance for pore fluid variations is extremely small. In particular, evaporation and condensation control are especially important for rapid aging at elevated temperature, where film production processes have heretofore apparently not been practically possible.

[0022] We have overcome the evaporation rate control problem by not attempting to actively control pore fluid vapor concentration above a wafer at all. Instead, the wafer is processed in an extremely low-volume chamber, such that through natural evaporation of a relatively small amount of the pore fluid contained in the wet gel film, the processing atmosphere becomes substantially saturated in pore fluid. Unless the wafer is cooled at some point in a substantially saturated processing atmosphere, this method also naturally avoids problems with condensation, which should generally be avoided, particularly during high temperature processing.

[0023] A metal-based nanoporous aerogel precursor sol is disclosed herein. This nanoporous aerogel precursor sol comprises a metal-based aerogel precursor reactant and a first solvent comprising a first polyol; wherein, the molar ratio of the first solvent molecules to the metal atoms in the reactant is at least 1 : 16. Preferably, the first polyol is glycerol. Preferably, the aerogel precursor reactant may be selected from the group consisting of metal alkoxides, at least partially hydrolyzed metal alkoxides, particulate metal oxides, and combinations thereof. Typically, the molar ratio of the first solvent molecules to the metal atoms in the reactant is no greater than 12 : 1, and preferably, the molar ratio of the first solvent molecules to the metal atoms in the reactant is between 1 : 2 and 12 : 1. In some embodiments, the molar ratio of the first solvent molecules to the metal atoms in the reactant is between 2.5 : 1 and 12 : 1. In this method, it is also preferable that the nanoporous dielectric has a porosity greater than 60% and an average pore diameter less than 25 nm. In some embodiments, the aerogel precursor also comprises a second solvent. Preferably, the second solvent has a boiling point lower than glycerol's. In some embodiments, the second solvent may be ethanol. In some embodiments, the first solvent also comprises a glycol, preferably selected from the group consisting of ethylene glycol, 1,4 butylene glycol, 1,5 pentanediol, and combinations thereof. In some embodiments, the first polyol is selected from the group consisting of 1,2,4-butanetriol; 1,2,3-butanetriol; 2-methyl-propanetriol; and 2-(hydroxymethyl)-1,3-propanediol; 1,4, 1,4, butanediol; and 2-methyl-1,3-propanediol, and combinations thereof. In some embodiments, the first polyol is a glycol selected from the group consisting of ethylene glycol, 1,4 butylene glycol, 1,5 pentanediol, and combinations thereof.

[0024] Thus, this invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, aged, and dried without atmospheric controls. In another aspect, this invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, rapidly aged at an elevated temperature, and dried with only passive atmospheric controls, such as limiting the volume of the aging chamber.

[0025] A method for forming a thin film nanoporous dielectric on a semiconductor substrate is disclosed herein. This method comprises the steps of providing a semiconductor substrate and depositing an nanoporous aerogel precursor sol upon the substrate. This aerogel precursor sol comprises a metal-based aerogel precursor reactant and a first solvent comprising glycerol; wherein, the molar ratio of the molecules of glycerol to the metal atoms in the reactant is at least 1 : 16. The method further comprises allowing the deposited sol to create a gel, wherein the gel comprises a porous solid and a pore fluid; and forming a dry, nanoporous dielectric by removing the pore fluid in a drying atmosphere without substantially collapsing the porous solid. In this method, the pressure of the drying atmosphere during the forming step is less than the critical pressure of the pore fluid, preferably near atmospheric pressure.

[0026] Preferably, the aerogel precursor reactant may be selected from the group consisting of metal alkoxides, at least partially hydrolyzed metal alkoxides, particulate metal oxides, and combinations thereof. Preferably, the aerogel precursor reactant comprises silicon. In some embodiments, the aerogel precursor reactant is TEOS. Typically, the molar ratio of the molecules of glycerol to the metal atoms in the reactant is no greater than 12 : 1, and preferably, the molar ratio of the molecules of glycerol to the metal atoms in the reactant is between 1 : 2 and 12 : 1. In some embodiments, the molar ratio of the molecules of glycerol to the metal atoms in the reactant is between 2.5 : 1 and 12 : 1. In this method, it is also preferable that the nanoporous dielectric has a porosity greater than 60% and an average pore diameter less than 25 nm. In some embodiments, the aerogel precursor also comprises a second solvent. Preferably,

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terminated by the solid:liquid ratio in the film at the gel time. It has now been discovered that the following criteria are desirable for aerogel thin film deposition, particularly where the thin film is required to planarize and/or gap fill a patterned wafer:

- 1) an initial viscosity suitable for spin-on application
- 2) stable viscosity at deposition
- 3) stable film thickness at gel time
- 4) a predetermined solid:liquid ratio at gel time
- 5) gelation shortly after deposition

No prior art precursor sol and method have been found which meet these conditions. However, in accordance with the present invention, it has now been found that a sol prepared with at least two solvents in specific ratios may be used to meet these conditions.

The method of depositing and gelling such a precursor sol can be best understood with reference to Figure 15.

[0050] As shown in Figure 15 for time $t=0$, a multi-solvent precursor sol may be spun onto a wafer at an initial film thickness D_0 and an initial viscosity h_0 . This is preferably done in a controlled atmosphere having a partial pressure of the low volatility solvent which greatly retards evaporation of the low volatility solvent from the wafer. Thus after spin-on application, the high volatility solvent is preferentially removed from the wafer during evaporation time period T_1 while the low volatility solvent is maintained, thereby decreasing the film thickness to D_1 . Viscosity also changes during this time to h_1 , preferably due primarily to the removal of solvent. Ideally, little cross-linking of polymeric clusters in the sol occurs during this time. At the end of T_1 , substantially all of the high volatility solvent should be evaporated, at which time film thickness should stabilize or proceed to shrink at a much reduced rate, thereby providing a predetermined liquid:solid ratio and thickness for the thin film at gel time.

[0051] Time period T_2 has the primary purpose of providing separation between the endpoint of evaporation time period T_1 and the gel point which occurs during gelation time period T_3 . Preferably, time period T_2 is greater than 0. However, some precursors, particularly those with solvents such as glycerol, that promote faster gelation, will gel toward the end of period T_1 . Additionally, during time period T_1 or T_2 a vapor-phase catalyst such as ammonia may be introduced into the controlled atmosphere. This catalyst may diffuse into the thin film, further activating the sol and promoting rapid cross-linking. Although little or no evaporation preferably takes place during T_2 , viscosity should begin to increase substantially as cross-linking continues to link polymeric clusters.

[0052] Evaporation after the gel point may result in poor gap-fill and planarity for patterned wafers. Consequently, after gelation time period T_3 , film thickness is preferably held nearly constant until the gel point has passed by limiting evaporation. Sometime during time period T_3 , a marked change in viscosity occurs as the sol nears the gel point, where large polymeric clusters finally join to create a spanning cluster which is continuous across the thin film.

[0053] Several advantages of this new approach are apparent from Figure 15. Sol viscosity and film thickness are both allowed to change rapidly, but generally not at the same time. Also, film thickness is changed from a first known value to a second known value which can be independently set by solvent ratios and spin conditions. Using this method, a low viscosity film may be applied, quickly reduced to a preset thickness, and rapidly gelled at a desired density.

[0054] The preceding paragraphs teach a method of varying the precursor sol viscosity independently of the dried gel density. However, it still leaves open the question of which solvents are most appropriate. Our experience shows that the solvent evaporation rate for traditional aerogel solvents is very sensitive to small changes in the vapor concentration and temperature. In an effort to better understand this process, we have modeled isothermal solvent vaporization from a wafer as a function of percent saturation. This modeling is based on mass transfer theory. Transport Phenomena, (particularly Chapters 16 and 17) by R. B. Bird, W. E. Stewart, and E. N. Lightfoot, is a good reference for mass transfer theory. These calculations were performed for a range of solvents. The ambient temperature evaporation rates for some of these solvents are given in Figure 1. For evaporation to not be a processing problem, the product of the evaporation rate and processing time (preferably on the order of minutes) should be significantly less than the film thickness. This suggests that for solvents such as ethanol, the atmosphere above the wafer would have to be maintained at over about 99% saturation. However, there can be problems associated with allowing the atmosphere to reach saturation or supersaturation. Some of these problems are related to condensation of an atmospheric constituent upon the thin film. Condensation on either the gelled or ungelled thin film has been found to cause defects in an insufficiently aged film. Thus, it is generally desirable to control the atmosphere such that no constituent is saturated.

[0055] Rather than using a high volatility solvent and precisely controlling the solvent atmosphere, we have discovered

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High optical clarity of bulk samples (This is likely due to a narrow pore size distribution)

[0063] Low density -- With this invention, it is possible to form dried gels at very low densities without pre-drying surface modification or supercritical drying. These low densities can generally be down around .3 to .2 g/cm³ (non-porous SiO₂ has a density of 2.2 g/cm³), or with care, below .1 g/cm³. Stated in terms of porosity (porosity is the percentage of a structure which is hollow), this denotes porosities of about 86% and 91% (about 95% porosity with a density of .1 g/cm³). As shown in Figure 3, these porosities correspond to dielectric constants of about 1.4 for the 86% porous, and 1.2 for 91% porous. The actual mechanism that allows these high porosities is not fully known. However, it may be because the gels have high mechanical strength, because the gels do not have as many surface OH (hydroxyl) groups, a combination of these, or some other factors. This method also seems to obtain excellent uniformity across the wafer.

[0064] If desired, this process can be adjusted (by varying the TEOS/solvent ratios) to give any porosity from above 90% down to about 50%. Typical prior art dried gels with small pore sizes required either supercritical drying or a surface modification step before drying to achieve these low densities. While some prior art xerogels have porosities greater than 50%; these prior art xerogels had substantially larger pore sizes (typically above 100 nm). These large pore size gels have significantly less mechanical strength. Additionally, their large size makes them unsuitable for filling small (typically less than 1 μm) patterned gaps on a microcircuit. If desired, this process can also be adjusted (by varying the TEOS/solvent ratios) to provide porosities below 50%. Porosities down to 20% are possible when care is taken to prevent premature gelation.

[0065] Thus, this invention has enabled a new, simple nanoporous low density dielectric fabrication method. This new glycerol-based method allows both bulk and thin film aerogels to be made without supercritical drying, or a surface modification step before drying. Prior art aerogels have required at least one of these steps to prevent substantial pore collapse during drying. Density Prediction - By varying the ratio of glycerol to silicon (or other metal), the density after drying can be accurately predicted. This accuracy is likely due to the well controlled evaporation allowed by the low volatility glycerol solvent. As our process shows excellent shrinkage control during aging and drying, this allows accurate prediction of the density (and thus porosity) of the dried gel. Although density prediction had not generally been considered a large problem with bulk gels, it had typically been difficult to predict the final porosity of thin film gels. This accurate density prediction, even for low porosity dried gels, is one reason why this new process might be preferred over existing xerogel processes for forming low porosity gels.

[0066] Simplified Aging -- We have found that in the production of nanoporous dielectrics it is preferable to subject the wet gel thin film to a process known as aging. Hydrolysis and condensation reactions do not stop at the gel point, but continue to restructure, or age, the gel until the reactions are purposely halted. It is believed that during aging, preferential dissolution and redeposition of portions of the solid structure produce beneficial results. These beneficial results include higher strength, greater uniformity of pore size, and a greater ability to resist pore collapse during drying. However, aging a wet gel in thin film form is difficult, as the film contains an extremely small amount of pore fluid that should be held fairly constant for a period of time in order for aging to occur. If pore fluid evaporates from the film before aging has strengthened the network, the film will tend to densify in xerogel fashion. On the other hand, if excess pore fluid condenses from the atmosphere onto the thin film before the network has been strengthened, this may locally disrupt the aging process and cause film defects.

[0067] Our new, glycerol-based process has radically simplified aging of thin film nanoporous dielectrics. Other thin film nanoporous dielectric aging processes have either allowed significant evaporation, fluid condensation, or required a controlled aging atmosphere. During deposition and gelation, at least to some degree, these glycerol-based processes behave similarly to the ethylene glycol-based processes described below. However, the ethylene glycol-based gels typically require atmospheric controls to prevent significant evaporation during aging, even at room temperature. In contrast, the glycerol-based gels have dramatically lower evaporation and shrinkage rates during aging. This allows atmospheric control to be loosened or eliminated during aging. We can fabricate high quality, thin film, glycerol-based nanoporous dielectrics with only passive atmospheric controls during room temperature or high temperature aging.

[0068] Shorter Gel Times -- The use of glycerol also substantially shortens the gel time. Many typical ethanol-based precursors have gel times of at least 400 seconds, when catalyzed (much longer w/o catalysis). However, we discovered that some glycerol-based precursors will gel during wafer spin-on, even without catalysis. This quick gelation is not only faster than an ethanol-based gel, but also surprisingly faster than an ethylene glycol-based gel. Figure 4 shows gel times for two different ethylene glycol-based compositions as a function of the amount of ammonia catalyst used. These gel times are for bulk gels for which there is no evaporation of ethanol and/or water as there would be for thin films. Evaporation increases the silica content and thus, decreases the gel time. Therefore, these gel times may be the upper limit for a given precursor/catalyst. The gel times reported in Figure 4 are approximately an order of magnitude shorter than conventional ethanol-based precursors. Gel times generally also exhibit a first order dependence on the concentration of ammonia catalyst. This implies that it may be possible to easily control the gel time.

[0069] For thin films of these new glycerol-based gels, it is routine to obtain gelation within seconds, even without a

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volume of the aging chamber.

Table 1

Approximate Aging Time as a Function of Temperature For Some Thin Film Glycerol-Based Gels	
Aging Temperature (Degrees C)	Aging Time For Glycerol-Based Gels (Order of Magnitude Approximations)
25	1 day
100	5 minutes
140	1 minute

Table 2

Approximate Thickness Loss During Aging vs. Saturation Ratio.									
Aging Time/ Temperature	Thickness Loss During Aging								
	Ethanol-Based Gel			EG-Based Gel			Glycerol-Based Gel		
	% Saturation			% Saturation			% Saturation		
	0%	50%	99%	0%	50%	99%	0%	50%	99%
1 day/25° C	8 mm	7 mm	86 µm	17 µm	7 µm	172 nm	13 nm	5 nm	.1 nm
300 sec/100° C	—	—	—	3 µm	1.2 µm	90 nm	600 nm	420 nm	9 nm
60 sec/140° C	—	—	—	—	—	—	6 µm	3 µm	60 nm

[0076] Improved yield and reliability considerations may require thickness losses below 2%, such as less than .5% or .1%. By using passive atmospheric control, this invention can be extended to these, and even lower evaporation losses. This passive control involves placing the gel in a relatively small closed container, at least during aging. In this aspect of the invention, evaporation from the wafer acts to raise the saturation ratio of the atmosphere inside the closed container. At any given temperature, this evaporation continues until the partial pressure of the vapor increases enough to equal the vapor pressure of the liquid. Thus, solvent/temperature combinations with lower vapor pressure will not allow as much liquid solvent to evaporate as a higher vapor pressure combination allows. Figure 8 shows how vapor pressure varies with temperature for several solvents. If the container size is known, the amount of evaporation can be calculated. Figure 9 shows an estimate of how thick of layer of solvent could potentially be evaporated if a 70% porous gel is placed in a 5 mm high cylindrical container that is the same diameter as the wafer. Figure 10 shows a similar estimate for a container with a 1 mm high airspace above the wafer. These figures show that, with a 5 mm high airspace, the 20 nm preliminary goal is feasible up to 120 degrees C for glycerol-based gels, but only up to 50 degrees C for ethylene glycol-based gels. With the 1 mm airspace, the 20 nm goal is feasible all the way up to 150 degrees C for the glycerol-based gels, but only up to 80 degrees C for the ethylene glycol-based gels. Of course, lower temperature processing allows less evaporation. Passive evaporation control using the 1 mm containers allows less than 1 nm of thickness loss (.1% of a 1µm thick film) for the glycerol-based gels, even at 100 degrees C.

[0077] There are many variations on this passive control approach. One variation allows the container size to increase. The thickness loss will linearly increase with the container volume. However, even a 1000 cubic centimeter container typically allows only 5 nm of glycerol evaporation at 80 degrees C. Another variation is the gel porosity. Higher porosity gels generally experience greater thickness losses while lower porosity gels generally experience slightly smaller thickness losses.

[0078] One disadvantage of glycerol is its relatively high viscosity which can cause problems with gap-filling and/or planarization. As described above, a low viscosity, high volatility solvent can be used to lower the viscosity. Figure 11A shows the calculated viscosity of some ethanol/glycerol and methanol/glycerol mixtures at room temperature. As the figure shows, alcohol can significantly reduce the viscosity of these mixtures. Figure 11B shows the calculated viscosity of some ethanol/ethylene glycol and methanol/ethylene glycol mixtures at room temperature. As this figure shows, the ethylene glycol is much less viscous than the glycerol, and small quantities of alcohol significantly reduce the viscosity of these mixtures. Also, if the viscosity using ethanol in the stock solution is higher than desired, further improvement can be realized by employing methanol in the precursor solution. The viscosities reported in Figures 11A-11B are for pure fluid mixtures only. In fact, depending upon the film precursor solution, the precursor solution might contain glycerol, alcohol, water, acid and partially react metal alkoxides. Of course, the viscosity can be increased before dep-

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larger ratios typically found in devices with small feature sizes.

[0086] In accordance with a first embodiment of the present invention, mix 61.0 mL tetraethoxysilane (TEOS), 61.0 mL glycerol, 4.87 mL water, and .2 mL 1M HNO₃ and reflux for 1.5 hours at ~ 60°C to form a stock solution. Equivalently, mix .27 mol TEOS, .84 mol glycerol, .27 mol water, and 2.04E-4 mol HNO₃ and reflux for 1.5 hours at ~ 60°C. After the stock solution is allowed to cool, the solution may be diluted with ethanol to reduce the viscosity. One suitable stock solution:solvent volume ratio is 1:8. However, this ratio will depend upon desired film thickness, spin speed, and substrate. This is mixed vigorously and typically stored in a refrigerator at ~ 7°C to maintain stability until use. The solution is typically warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that has no special control of solvent saturation (e.g., in a cleanroom with non-exotic humidity controls). During and after this deposition and spinning, the ethanol, water, and the nitric acid are evaporating from film 14, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation temporarily cools the thin film, although the film temperature rises within seconds after the evaporation rate drops off. This cooling retards, but does not prevent gelation. This evaporation also shrinks thin film 14 and concentrates the silica content of the sol, forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the ethanol has been removed. This concentrating, evaporative basification, and/or rewarming of the film typically cause gelation within seconds.

[0087] Film 18 has an approximately known ratio of silicon to pore fluid at the gel point. This ratio is approximately equal to the ratio of TEOS to glycerol in the as-deposited sol (with minor changes due to remaining water, continued reactions and incidental evaporation). As this method largely prevents the gel from permanently collapsing, this ratio determines the density of the aerogel film that will be produced from the sol thin film.

[0088] After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures, e.g., about a day at room temperature. It should be noted that the pore fluid changes somewhat during processing. These changes may be due to continued reactions, evaporation/condensation, or chemical additions to the thin film. Aging may preferably be accomplished by letting the substrate and gel sit for approximately 24 hours at about 25° C or by heating it to 130-150° C for about 1 minute in a closed container.

[0089] Aged film 18 may be dried without substantial densification by one of several methods. However, with these new glycerol-based gels, one alternative is to use a solvent exchange to replace the aging fluid with a drying fluid and then air dry the film 18 from this drying fluid. This drying method uses a solvent exchange to replace the aging fluid with a different fluid. Whether this fluid is identical to the aging fluid or not, the pore fluid that is present during drying is sometimes referred to as "drying fluid". If used, the solvent exchange replaces the aging fluid that is dominated by the glycerol and its associated high surface tension with a drying fluid that has a lower surface tension. This solvent exchange may be carried out as a one or two step process. In the two step process, the first step replaces the aging fluid with an intermediate by dispensing approximately 3-8 mL of ethanol at room temperature (or warmer) onto aged thin film 18, then spinning the wafer between approximately 50 and 500 rpm for about 5-10 seconds. It sometimes requires between 3 and 6 spin-on sequences to replace most of the aging fluid. The second step preferably replaces the intermediate fluid with a drying fluid such as heptane. This step preferably comprises dispensing approximately 3-8 mL of heptane at room temperature (or warmer) onto aged thin film 18, then spinning the wafer between approximately 50 and 500 rpm for about 5-10 seconds. It sometimes requires between 3 and 6 spin-on sequences to replace most of the intermediate fluid. This solvent exchange method allows us to remove nearly all the glycerol-containing fluid before drying. The drying fluid (heptane in this case) is finally allowed to evaporate from the wet gel 18, forming a dry nanoporous dielectric (dried gel). If the film can be satisfactorily dried from a liquid that is soluble with the aging fluid, the intermediate may not be required. In many cases, the wet gel can be dried directly from ethanol, or other suitable solvent.

[0090] This evaporation may be performed by exposing the wafer surface to an atmosphere that is not near saturated with the drying fluid. For example, the wafer could be in a substantially uncontrolled atmosphere, or a drying gas could be introduced into the atmosphere. To prevent boiling, drying should preferably start at a temperature somewhat below the boiling point of the drying fluid, such as room temperature. If a higher boiling point drying fluid, such as glycerol, is used (e.g., drying without solvent replacement), the starting drying temperature can be increased to a temperature near or equal to the aging temperature. As the thin film becomes predominately dry (typically within seconds), the temperature should then be increased above the boiling point of both the aging fluid and the drying fluid. This method prevents destructive boiling, yet insures that all fluid is removed. Glycerol, as well as some other fluids, either decompose at approximately the same temperature as they boil, or decompose in lieu of boiling. With these fluids, particularly fluids like glycerol that can decompose into toxic substances, care should be taken not to overheat the evaporated fluid or the undried wafer. After drying, it is preferable to bake the nanoporous dielectric for a short time (such as 300° for 15 to 60 minutes) to help remove any residual materials, such as organics, that are in or on the dielectric. The

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Table 3. (continued)

Substance Summary			
Ref #	Specific Example	Functional Description	Preferred Alternatives
5	Aging fluid	Drying Fluid	Heated aging fluid, heptane, acetone, isopropanol, ethanol, methanol, 2-ethylbutyl alcohol, alcohol/water mixtures, ethylene glycol, other liquids that are miscible with the aging fluid, yet have lower surface tension than the aging fluid, combinations thereof.
10			
15	Hexamethyldisilazane (HMDS)	Surface Modification Agent	hexaphenyldisilazane, trimethylmethoxysilane, dimethyldimethoxysilane, trimethylchlorosilane (TMCS), phenyl compounds and fluorocarbon compounds.
20			

[0093] In accordance with a second, higher density, embodiment of the present invention, mix 150.0 mL TEOS, 61.0 mL glycerol, 150.0 mL ethanol, 12.1 mL water, and .48 mL 1M HNO₃ and reflux for 1.5 hours at ~ 60°C to form a stock solution. Equivalently, mix .67 mol TEOS, .84 mol glycerol, 2.57 mol ethanol, .67 mol water, and 4.90E-4 mol HNO₃ and reflux for 1.5 hours at ~ 60°C. After the stock solution is allowed to cool, the solution may be diluted with ethanol to reduce the viscosity. One suitable stock solution:solvent volume ratio is 1:8. This is mixed vigorously and typically stored in a refrigerator at ~ 7°C to maintain stability until use. The solution is warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that is not solvent controlled (e.g., standard exhausts in a cleanroom with non-exotic humidity controls). During and after this deposition and spinning, ethanol (a viscosity reduction additive and a reaction product from the TEOS and water) and water is evaporating from film 14, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation shrinks thin film 14 and concentrates the silica content of the sol forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the water has been removed. This concentrating typically causes gelation within minutes.

[0094] Further processing generally follows the process described in the first embodiment. After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures. Aged film 18 may be dried without substantial densification by one of several methods. However, with the lower density formulations of these new glycerol-based gels, it is preferable to perform a non-supercritical drying, such as a solvent exchange followed by air drying the film 18 from the drying fluid, as described in the first embodiment. The nanoporous dielectric can then be subjected to a post-dry bake and/or a surface modification, as described in the first embodiment. The theoretical dielectric constant (before surface modification) of this embodiment is 1.8.

[0095] In accordance with a third, higher density, embodiment of the present invention, mix 208.0 mL TEOS, 61.0 mL glycerol, 208.0 mL ethanol, 16.8 mL water, and .67 mL 1M HNO₃ and reflux for 1.5 hours at ~ 60°C to form a stock solution. Equivalently, mix .93 mol TEOS, .84 mol glycerol, 3.56 mol ethanol, .93 mol water, and 6.80E-4 mol HNO₃ and reflux for 1.5 hours at ~ 60°C. After the stock solution is allowed to cool, the solution may be diluted with ethanol to reduce the viscosity. One suitable stock solution:solvent volume ratio is 1:8. This is mixed vigorously and typically stored in a refrigerator at ~ 7°C to maintain stability until use. The solution is warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that is not solvent controlled (e.g., standard exhausts in a cleanroom with non-exotic humidity controls). During and after this deposition and spinning, ethanol and water is evaporating from film 14, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation shrinks thin film 14 and concentrates the silica content of the sol forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the water has been removed. This concen-

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[0101] Other ratios of solvent to reactant ratios can be used to provide different porosities/dielectric constants. Figure 14 shows the theoretical relationship between the molar ratio of glycerol molecules to metal atoms and the porosity of a nanoporous dielectric for the case where all ethanol is evaporated from the deposited sol. Typically, the higher porosity glycerol-based gels (generally less than about .51 g/cc) prefer a solvent exchange or other method to lessen shrinkage during drying. On the other hand, the lower porosity gels require care to prevent early gelation. This may comprise pH adjustment, temperature control, or other methods known in the art. In some applications, it is also permissible to allow high volatility solvent evaporation after gelation.

[0102] As described above, the higher density glycerol-based gels (generally greater than about .64 g/cc) can be aged and dried with little shrinkage, even without a solvent exchange. An unaged wafer may be placed in a small volume furnace, or a small container, which can go on a hot plate. After an optional evacuation, the container is sealed at room temperature. The container remains sealed as the temperature is ramped up, quickly aging the film, and lowering the aging/drying fluid viscosity. After sufficient aging (possibly during the temperature ramp), the gel is ready for drying. At temperatures near glycerol's boiling point, the glycerol viscosity can be low enough (compared to the strength of an aged film of the predetermined porosity), that the glycerol in the furnace atmosphere can be removed and the film directly dried. Note that, in the most demanding low density applications, a somewhat lower surface tension can be obtained by increasing the drying temperature above the boiling point of glycerol. In these cases, the furnace needs to withstand the pressure (most sub-critical drying situations can be handled with pressures under 1 to 3 MPa). Additionally, care needs to be taken that the glycerol in the furnace atmosphere is, especially at first, slowly removed. The glycerol in the furnace atmosphere may be removed, e.g., by bleeding off the pressure, by a vacuum pump, or by sweeping the glycerol off with a gas. The furnace temperature may be held constant or continue to be raised while the glycerol is being removed (the furnace may be ramped on up to the bake temperature while sweeping the glycerol off with the gas). While some glycerol can be introduced during heating to minimize evaporation from the film, preferably the furnace volume is low enough that evaporation does not significantly reduce film thickness even without the introduction of glycerol during heating. If a film requires supercritical drying, perhaps to eliminate even temporary shrinkage, it is preferable to use a CO₂ solvent exchange as is well known in the art.

[0103] Although the same stock solutions can be used for bulk aerogels as thin film aerogels, the processing is substantially different. With different stock solution mixtures, the following example can be adapted to provide bulk gels with different porosities. In accordance with a bulk aerogel embodiment of the present invention, mix 208.0 mL TEOS, 61.0 mL glycerol, 208.0 mL ethanol, 16.8 mL water, and .67 mL 1M HNO₃ and reflux for 1.5 hours at ~ 60°C to form a stock solution. Equivalently, mix .93 mol TEOS, .84 mol glycerol, 3.56 mol ethanol, .93 mol water, and 6.80E-4 mol HNO₃ and reflux for 1.5 hours at ~ 60°C. This is typically stored in a refrigerator at ~ 7°C to maintain stability until use. The stock solution is preferably warmed to room temperature prior to placing into molds. After pouring into molds, the ethanol, water, and acid is allowed to evaporate, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation reduces the volume of the stock solution precursor sol and concentrates the silica content of the sol. It is allowable for at least some of the evaporation to occur before filling the mold. This pre-fill evaporation might be especially useful if the configuration of the mold does not lend itself to substantial evaporation after filling, such as a low exposed surface area mold or a mold configuration that is incompatible with shrinkage. Although this evaporation is not required, it has several advantages, including faster gelation without a catalyst and less shrinkage after gelation.

[0104] After this evaporation, the sol has an approximately known ratio of silicon to pore fluid at the gel point. This ratio is approximately equal to the ratio of TEOS to glycerol in the precursor mix (with minor changes due to remaining water, continued reactions and incidental evaporation). As this method largely prevents the gel from permanently collapsing, this ratio determines the density of the aerogel that will be produced. If the sol does not gel during evaporation, this sol will gel soon after substantially all of the water, ethanol, and acid has evaporated.

[0105] Alternatively, one may catalyze the precursor with .5M ammonium nitrate before filling the mold. With this mixture, the sol typically gels in minutes. Remove the wet gel from the mold and allow the ethanol and water to evaporate. Typically, the gel will shrink during this evaporation. However, as with the other approaches, when the evaporation is substantially complete, the sol has an approximately known ratio of silicon to pore fluid at the gel point. This ratio is approximately equal to the ratio of TEOS to glycerol in the precursor mix (with minor changes due to remaining water, continued reactions and incidental evaporation). As this method largely prevents the gel from permanently collapsing, this ratio determines the density of the aerogel that will be produced.

[0106] After gelation, the wet gel comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures. Aging may preferably be accomplished by letting the substrate and gel sit for approximately 24 hours at about 25° C or by heating it to 130-150° C for about 5 minutes in a closed container. These high temperature aging parameters are valid for a 5 mm diameter bulk aerogel. However, due to the wet gel's low thermal conductivity, the high temperature accelerated aging time and temperature combinations are highly dependent upon the configuration of the bulk gel.

[0107] After this initial aging, remove the gel from the molds and dry directly from the mother liquor (that is, the pore

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of the sol forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the water has been removed. This concentrating typically causes gelation within minutes.

[0115] After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures, e.g., about a day at room temperature. It should be noted that the pore fluid changes somewhat during processing. Aging may preferably be accomplished by letting the device sit in a low volume aging chamber for approximately 5 minutes at about 100 degrees C.

[0116] Aged film 18 may be dried without substantial densification by one of several methods, including a solvent exchange followed by air drying. However, it is preferable to air dry the film 18 from the aging fluid, as described in the third glycerol embodiment. The nanoporous dielectric can then be subjected to a post-dry bake and/or a surface modification, as described in the first glycerol embodiment.

[0117] The discussion to this point has shown some of the advantages of aging in a closed container. Since suitable aging chambers do not seem to exist, we will describe the chambers we have invented to implement this process. One embodiment of aging container is illustrated in Figures 16A, 16B and 16C. In this embodiment, a processing apparatus comprises a body 20, having a substantially planar plate 22 with a resilient seal 24 attached thereto. Plate 22 need only be planar to the extent necessary to provide clearance with a thin film during operation, and may be constructed of any material compatible with the underlying process (e.g., semiconductor fabrication), although materials with high thermal conductivity, such as stainless steel, glass, or aluminum are preferred. Resilient seal 24 should preferably be designed to withstand wet gel processing temperatures and pore fluids; many suitable materials, including TEFLON- and neoprene-based materials, are known to those of ordinary skill in the art. Depending on the nature of temperature control used in the apparatus; it may be preferable to have seal 24 be either substantially thermally insulating or thermally conductive.

[0118] In operation, body 20 may simply be rested on a substrate 26, as shown in Figure 16C. This substrate may be an optical substrate, such as glass or plastic, or a semiconductor substrate, such as a Si wafer. In this embodiment, seal 24 functions both as an atmospheric seal and as a spacer which sets the volume of chamber 32 formed by substrate surface 28, chamber surface 30 and seal 24. For example, seal 24 may be designed to compress to a thickness of about 1 mm under the weight of plate 22, thus creating chamber 32 with a 1 mm height when body 20 is placed on substrate 26. For many thin film applications, chamber 32 need only be substantially sealed, as some small degree of vapor leakage over the course of processing substrate 26 will not appreciably affect the final film properties.

[0119] Body 20 finds application at many points in an aerogel thin film process. It may be used to limit evaporation before a sol film has gelled, as an aging chamber for wet gel thin films, as a storage or transport chamber for such films, or as a drying chamber. In all of these applications, it is recognized that both sol and gel thin films contain extremely small amounts of liquid, such that a chamber of limited volume is necessary to prevent substantial evaporation from the film.

[0120] In another embodiment, body 20 may comprise more elements, as shown in Figures 17A and 17B. In this embodiment, body 20 additionally comprises a substrate holder 36 and substrate temperature control means 34. This embodiment shows the additional aspect of a seal 24 located outboard of the substrate (or in some cases seal 24 may even be deleted), such that a thin film may be formed on the entirety of substrate surface 28. When chamber 32 is closed, planar plate 22 and wafer holder 36 may be thermally coupled such that temperature control means 34 may be used to simultaneously regulate the temperature of body 20, substrate 26 and chamber 32.

[0121] In another embodiment shown in Figures 18A and 18B, seal 24 provides some degree of thermal isolation between planar plate 22 and wafer holder 36. This allows temperature control means 34 to control substrate temperature, while separate temperature control means 38 are used to control planar plate temperature. Such an embodiment may have an advantage for drying a wet gel film, as the temperature of planar plate 22 can be selectively lowered to promote condensation on chamber surface 30.

[0122] Figures 19A, 19B and 19C show additional aspects of these aging chambers. For example, in Figure 19A, substrate 26 is shown being processed in an inverted position. In this embodiment, accidental or purposeful condensation onto chamber surface 30 may be collected without the possibility of such condensation dropping onto substrate surface 26. In Figure 19B, not only is substrate 26 processed inverted, but a first solvent layer 42 (preferably of the same composition as at least one pore fluid) is dispensed, e.g., from a first solvent supply tube 40, onto chamber surface 30 prior to closing the chamber. In this embodiment, layer 42 may be used to help saturate the processing atmosphere, resulting in less evaporation of pore fluid from substrate 26.

[0123] In Figure 19C, an embodiment is shown wherein some atmospheric adjustment means 44 is connected through at least one port 46 (which may be closeable) to chamber 32. Atmospheric adjustment means 44 may be used to create a vacuum or to overpressurize chamber 32 as appropriate, or to exchange the atmosphere in chamber 32, or to supply a pore fluid vapor to chamber 32. This embodiment may be used, for example, to age a thin film at a temperature higher than the boiling point of a pore fluid, by operating chamber 32 at above atmospheric pressure. This embodiment may also be used to remove at least a portion of the pore fluid vapor from chamber 32 after aging, thereby

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temperature and humidity controls, although the wafer and/or precursor sol may have independent temperature controls. If this substantially uncontrolled atmosphere allows excessive vaporation, then either passive or less preferably, active atmospheric controls may be needed. For the purposes of this application, passive controls are limited to the placing the wafer in a relatively small container. This container may be partially or fully sealed and may or may not also contain a liquid reservoir of the solvent. However, the container will not have exotic environmental controls for the wafer, container atmosphere, and/or reservoir.

[0129] Another example of modification to the basic method is that, before drying (and generally, but not necessarily, after aging), the thin film wet gel 18 may have its pore surfaces modified with a surface modification agent. This surface modification step replaces a substantial number of the molecules on the pore walls with those of another species. If a surface modifier is applied, it is generally preferable to remove the water from the wet gel 18 before the surface modifier is added. The water can be removed by rinsing the wafer in pure ethanol, preferably by a low speed spin coating as described in the solvent exchange in the first embodiment example. This water removal is beneficial, because water will react with many surface modification agents, such as HMDS; however, it is not necessary. With our new glycerol-based method, surface modification need not be performed to help prevent pore collapse, but it can be used to impart other desirable properties to the dried gel. Some examples of potentially desirable properties are hydrophobicity, reduced dielectric constant, increased resistance to certain chemicals, and improved temperature stability. Some potential surface modifiers that may impart desirable properties include hexamethyldisilazane (HMDS), the alkyl chlorosilanes (trimethylchlorosilane (TMCS), dimethyldichlorosilane, etc.), the alkylalkoxysilanes (trimethylmethoxysilane, dimethyldimethoxysilane, etc.), phenyl compounds and fluorocarbon compounds. One useful phenyl compound is hexaphenyldisilazane. Some other useful phenyl compounds will typically follow the basic formula, $\text{Ph}_x\text{A}_y\text{SiB}_{(4-x-y)}$, where, Ph is a phenolic group, A is a reactive group such as Cl or OCH_3 , and B are the remaining ligands which, if there are two, can be the same group or different. Some examples of these phenyl surface modification agents include compounds with 1 phenolic group such as phenyltrichlorosilane, phenyltrifluorosilane, phenyltrimethoxysilane, phenyltriethoxysilane, phenylmethylchlorosilane, phenylethyldichlorosilane, phenyldimethylethoxysilane, phenyldimethylchlorosilane, phenyldichlorosilane, phenyl(3-chloropropyl)dichlorosilane, phenylmethylvinylchlorosilane, phenylethyldimethylchlorosilane, phenyltrichlorosilane, phenyltrimethoxysilane, phenyltris (trimethylsiloxy) silane, and phenylallyldichlorosilane. Other examples of these phenyl surface modification agents include compounds with 2 phenolic groups such as diphenyldichlorosilane, diphenylchlorosilane, diphenylfluorosilane, diphenylmethylchlorosilane, diphenylethyldichlorosilane, diphenyldimethoxysilane, diphenylmethoxysilane, diphenylethoxysilane, diphenylmethylmethoxysilane, diphenylmethylethoxysilane and diphenyldiethoxysilane. These phenyl surface modification agents also include compounds with 3 phenolic groups such as triphenylchlorosilane, triphenylfluorosilane, and triphenylethoxysilane. Another important phenyl compound, 1,3-diphenyltetramethyldisilazane, is an exception to this basic formula. These lists are not exhaustive, but do convey the basic nature of the group. The useful fluorocarbon based surface modification agents include (3,3,3-trifluoropropyl)trimethoxysilane, (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1 dimethylchlorosilane, and other fluorocarbon groups that have a reactive group, such as Cl or OCH_3 , that will form covalent bonds with a hydroxyl group.

[0130] The paragraph above lists some of the typical useful properties for many conventional applications. However, there are other potential applications for nanoporous dielectrics and aerogels that may have different desirable properties. Examples of some other potentially desirable properties include hydrophilicity, increased electrical conductivity, increased dielectric breakdown voltage, increased or decreased reactivity with certain chemicals, and increased volatility. This list is not exhaustive. However, it shows that, depending upon the application, many different types of properties may be desirable. Thus, it is clear that many other materials that will form covalent bonds with hydroxyl groups are potential surface modifiers that may impart other potentially desirable properties.

[0131] This invention also comprises the use of gelation catalysts, such as ammonium hydroxide. This also includes the allowance of other gelation catalysts in place of the ammonium hydroxide and/or for the gelation catalyst to be added after deposition. Typically, these alternate catalysts modify the pH of the sol. It is preferable to use catalysts that raise the pH, although acid catalysts can be used. Typically, acid catalysis results in longer processing times and a denser dielectric than a base catalyzed process. Some examples of other preferred gelation catalysts include ammonia, the volatile amine species (low molecular weight amines) and volatile fluorine species. When the catalyst is added after deposition, it is preferable to add the catalyst as a vapor, mist, or other vaporish form.

[0132] This invention allows production of nanoporous dielectrics at room temperature and atmospheric pressure, without a separate surface modification step. Although not required to prevent substantial densification, this new method does not exclude the use of supercritical drying or surface modification steps prior to drying. To the extent that the freezing rates are fast enough to prevent large (e.g., 50 nm) crystals, it is also compatible with freeze drying. In general, this new method is compatible with most prior art aerogel techniques.

[0133] Other examples of modifications involve the reaction atmosphere and/or temperature. Also coating and gelation need not be performed in the same chamber or even in the same atmosphere. For instance, the substrate may have its temperature lowered to retard gelation or elevated to speed surface modification and/or gelation. Also, total pressure and/or temperature may be varied to further control evaporation rates and/or gel time. Elevated temperature

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is silicon.

12. The aerogel precursor sol according to any of claims 1 to 11, further comprising water.
- 5 13. The aerogel precursor sol according to any of claims 1 to 11, further comprising a second solvent which is different from the first solvent.
14. The aerogel precursor sol according to claim 13, wherein said second solvent is an alcohol.
- 10 15. The aerogel precursor sol according to claim 13, wherein said second solvent is ethanol.
16. The aerogel precursor sol according to any of claims 1 to 15, further comprising a pH modification agent.
17. The aerogel precursor sol according to any of claims 1 to 15, further comprising an acid.
- 15 18. The aerogel precursor sol according to claim 17, wherein said acid is nitric acid.
19. The aerogel precursor sol according to any of claims 1 to 15, wherein the pH of said sol is between 3 and 5.
- 20 20. The aerogel precursor sol according to any of claims 1 to 15, further comprising a gelation catalyst.
21. The aerogel precursor sol according to claim 20, wherein said gelation catalyst is ammonium hydroxide.
22. The aerogel precursor sol according to claim 20, wherein the pH of said sol is between 7 and 9.
- 25 23. The aerogel precursor sol according to any of claims 1 to 22, wherein the viscosity of said sol is between 1 and 12 centipoise.
24. The aerogel precursor sol according to any of claims 1 to 15, wherein the viscosity of said sol is between 1 and 5 centipoise.
- 30 25. The aerogel precursor sol according to any of claims 1 to 7, wherein said reactant is selected from the group consisting of pyrogenic silica, colloidal silica, and combinations thereof.
- 35 26. A non-supercritical method of forming a nanoporous aerogel, said method comprising the steps of:
 - providing an aerogel precursor sol as defined in any one of claims 1 to 25, said sol being dispersed in said first solvent and a second solvent,
 - 40 evaporating substantially all of said second solvent while preventing substantial evaporation of said first solvent, and allowing the sol to create a gel, wherein the gel comprises a porous solid and a pore fluid;
 - continuing to prevent substantial evaporation of said first solvent from said sol until a drying step,
 - 45 wherein said drying step comprises forming a dry aerogel by removing the pore fluid in a non-supercritical drying atmosphere without substantial collapse of the porous solid;
 - whereby the skeletal density of the dry aerogel is determined approximately by the volume ratio of said aerogel precursor reactant to said first solvent in said aerogel precursor sol.
 - 50
27. The method of claim 26, wherein said gel is created before said evaporating step completes.
28. The method of claim 26, wherein said drying step further comprises a solvent exchange.
- 55 29. The method of claim 26, further comprising aging said gel before said drying step.
30. The method of claim 29, wherein the aging step is without substantial evaporation of said first solvent.

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54. The method of claim 36, wherein the reactant is a metal alkoxide selected from the group consisting of tetraethoxysilane, tetramethoxysilane, methyltriethoxysilane, 1,2-Bis(trimethoxysilyl) ethane and combinations thereof.

55. The method of claim 36, wherein the reactant is tetraethoxysilane.

56. The method of claim 36, wherein the dry, porous aerogel has a porosity greater than 60%.

57. The method of claim 56, wherein the porosity is between 60% and 90%.

58. The method of claim 56, wherein the porosity is greater than 80%.

59. The method of claim 36, further comprising the step of replacing at least part of the pore fluid with a liquid before the removing of the pore fluid step.

60. The method of claim 59, wherein the liquid comprises hexanol.

61. The method of claim 36, further comprising the step of annealing the dry, porous aerogel.

62. The method of claim 36, wherein the pressure of the drying atmosphere is less than 3 MPa.

Patentansprüche

1. Metallhaltiges Vorläufersol für ein Aerogel mit einem Aerogelvorläufer-Reaktant, der aus der aus Metallalkoxiden, wenigstens teilweise hydrolysierten Metallalkoxiden, dispersen Metalloxiden und Kombinationen derselben bestehenden Gruppe ausgewählt ist, und mit einem Polyol als einem ersten Lösungsmittel, wobei das Polyol aus der aus Glycerol, Ethylenglycol, 1,4-Butylenglycol, 1,5-Pentandiol, 1,2,4-Butantriol, 1,2,3-Butantriol, 2-Methylpropantriol, 2-(Hydroxymethyl)-1,3-propandiol, 1,4,1-4-Butandiol, 2-Methyl-1,3-propandiol und Kombinationen derselben bestehenden Gruppe ausgewählt ist, wobei das Molverhältnis der Moleküle des ersten Lösungsmittels zu den Metallatomen in dem Reaktant mindestens 1:16 beträgt.

2. Vorläufersol für ein Aerogel nach Anspruch 1, bei dem das Polyol Glycerol ist.

3. Vorläufersol für ein Aerogel nach Anspruch 1, bei dem das erste Lösungsmittel Ethylenglycol ist.

4. Vorläufersol für ein Aerogel nach einem der Ansprüche 1 bis 3, bei dem das Molverhältnis der Moleküle des ersten Lösungsmittels zu den Metallatomen in dem Reaktant nicht größer ist als 12:1.

5. Vorläufersol für ein Aerogel nach einem der Ansprüche 1 bis 3, bei dem das Molverhältnis der Moleküle des ersten Lösungsmittels zu den Metallatomen in dem Reaktant zwischen 1:2 und 12:1 liegt.

6. Vorläufersol für ein Aerogel nach einem der Ansprüche 1 bis 3, bei dem das Molverhältnis der Moleküle des ersten Lösungsmittels zu den Metallatomen in dem Reaktant zwischen 1:4 und 4:1 liegt.

7. Vorläufersol für ein Aerogel nach einem der Ansprüche 1 bis 3, bei dem das Molverhältnis der Moleküle des ersten Lösungsmittels zu den Metallatomen in dem Reaktant zwischen 2,5:1 und 12:1 liegt.

8. Vorläufersol für ein Aerogel nach einem der Ansprüche 1 bis 7, bei dem der Reaktant ein Metallalkoxid ist, das aus der aus Tetraethoxysilan, Tetramethoxysilan, Methyltriethoxysilan, 1,2-Bis(trimethoxysilyl)ethan und Kombinationen derselben bestehenden Gruppe ausgewählt ist.

9. Vorläufersol für ein Aerogel nach einem der Ansprüche 1 bis 7, bei dem der Reaktant Tetraethoxysilan ist.

10. Vorläufersol für ein Aerogel nach Anspruch 9, bei dem das Tetraethoxysilan wenigstens teilweise hydrolysiert ist.

11. Vorläufersol für ein Aerogel nach einem der Ansprüche 1 bis 7, bei dem das Metall in dem Aerogelvorläufer-Reaktant Silicium ist.

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29. Verfahren nach Anspruch 26, bei dem ferner das Gel vor dem Trocknen gealtert wird.
30. Verfahren nach Anspruch 29, bei dem das Altern im wesentlichen ohne Verdampfen des ersten Lösungsmittels durchgeführt wird.
31. Verfahren nach einem der Ansprüche 26 bis 30, bei dem das zweite Lösungsmittel ein Reaktionsprodukt aus dem Schritt der Gelbildung umfaßt.
32. Verfahren nach einem der Ansprüche 26 bis 31, bei dem das zweite Lösungsmittel einen Dampfdruck hat, der mindestens zweimal so hoch ist wie der Dampfdruck des ersten Lösungsmittels.
33. Verfahren nach Anspruch 26, bei dem ferner eine dünne Schicht des Vorläufersols für ein Aerogel auf ein Substrat aufgebracht wird.
34. Verfahren nach Anspruch 33, bei dem das Substrat ein Halbleitersubstrat mit einem mikroelektronischen Schaltkreis ist.
35. Verfahren nach Anspruch 33 oder 34, bei dem das Aufbringen einer Dünnschicht das Aufschleudern des Vorläufersols für ein Aerogel auf das Substrat umfaßt.
36. Verfahren nach einem der Ansprüche 26 bis 35, bei dem das erste Lösungsmittel Glycerol umfaßt.
37. Verfahren nach einem der Ansprüche 26 bis 35, bei dem das Polyol ein Glycol ist.
38. Verfahren nach Anspruch 36, bei dem das nanoporöse Aerogel eine Porosität von mehr als 60 % und einen durchschnittlichen Porendurchmesser von weniger als 20 nm hat.
39. Verfahren nach Anspruch 36, bei dem das nanoporöse Aerogel eine Dielektrizitätskonstante von weniger als 2,0 hat.
40. Verfahren nach Anspruch 36, bei dem das nanoporöse Aerogel eine Dielektrizitätskonstante von weniger als 1,8 hat.
41. Verfahren nach Anspruch 36, bei dem das nanoporöse Aerogel eine Dielektrizitätskonstante von weniger als 1,4 hat.
42. Verfahren nach Anspruch 36, bei dem die Temperatur des Substrats während des Trocknens über der Gefrieretemperatur des Porenfluids liegt.
43. Verfahren nach Anspruch 42, bei dem im Verlauf des Verfahrens kein die Oberfläche modifizierendes Mittel vor dem Trocknen zugesetzt wird.
44. Verfahren nach Anspruch 43, bei dem das nanoporöse Aerogel eine Porosität von mehr als 60 % und einen durchschnittlichen Porendurchmesser von weniger als 20 nm hat.
45. Verfahren nach Anspruch 29, bei dem wenigstens ein Teil des Alterns in einem im wesentlichen geschlossenen Behälter durchgeführt wird.
46. Verfahren nach Anspruch 29, bei dem die Temperatur des Gels während des Alterns größer ist als 30°C.
47. Verfahren nach Anspruch 29, bei dem die Temperatur des Gels während des Alterns größer ist als 80°C.
48. Verfahren nach Anspruch 29, bei dem die Temperatur des Gels während des Alterns größer ist als 130°C.
49. Verfahren nach Anspruch 36, bei dem der poröse Feststoff während des Entfernens des Porenfluids weniger als 5 % abnehmende Volumenverringerung erfährt.
50. Verfahren nach Anspruch 36, bei dem der poröse Feststoff während des Entfernens des Porenfluids weniger als

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dites molécules d premier solvant aux atomes de métal dans l dit réactif, est de 2,5:1 à 12:1.

8. Sol de précurseur d'aérogel selon l'une quelconque des revendications 1 à 7, dans lequel ledit réactif est un alcoolate de métal choisi parmi le tétraéthoxysilane, le tétraméthoxysilane, le méthyl-triéthoxysilane, le 1,2-bis(triméthoxysilyl)éthane et leurs associations.
9. Sol de précurseur d'aérogel selon l'une quelconque des revendications 1 à 7, dans lequel ledit réactif est le tétraéthoxysilane.
10. Sol de précurseur d'aérogel selon la revendication 9, dans lequel ledit tétraéthoxysilane est au moins partiellement hydrolysé.
11. Sol de précurseur d'aérogel selon l'une quelconque des revendications 1 à 7, dans lequel le métal dans le réactif précurseur d'aérogel est le silicium.
12. Sol de précurseur d'aérogel selon l'une quelconque des revendications 1 à 11, comprenant en outre de l'eau.
13. Sol de précurseur d'aérogel selon l'une quelconque des revendications 1 à 11, comprenant en outre un deuxième solvant différent du premier solvant.
14. Sol de précurseur d'aérogel selon la revendication 13, dans lequel ledit deuxième solvant est un alcool.
15. Sol de précurseur d'aérogel selon la revendication 13, dans lequel ledit deuxième solvant est l'éthanol.
16. Sol de précurseur d'aérogel selon l'une quelconque des revendications 1 à 15, comprenant en outre un agent de modification de pH.
17. Sol de précurseur d'aérogel selon l'une quelconque des revendications 1 à 15, comprenant en outre un acide.
18. Sol de précurseur d'aérogel selon la revendication 17, dans lequel ledit acide est l'acide nitrique.
19. Sol de précurseur d'aérogel selon l'une quelconque des revendications 1 à 15, dans lequel le pH dudit sol est de 3 à 5.
20. Sol de précurseur d'aérogel selon l'une quelconque des revendications 1 à 15, comprenant en outre un catalyseur de gélification.
21. Sol de précurseur d'aérogel selon la revendication 20, dans lequel ledit catalyseur de gélification est l'hydroxyde d'ammonium.
22. Sol de précurseur d'aérogel selon la revendication 20, dans lequel le pH dudit sol est de 7 à 9.
23. Sol de précurseur d'aérogel selon l'une quelconque des revendications 1 à 22, dans lequel la viscosité dudit sol est de 1 à 12 centipoises.
24. Sol de précurseur d'aérogel selon l'une quelconque des revendications 1 à 15, dans lequel la viscosité dudit sol est de 1 à 5 centipoises.
25. Sol de précurseur d'aérogel selon l'une quelconque des revendications 1 à 7, dans lequel ledit réactif est choisi parmi la silice pyrogène, la silice colloïdale et leurs associations.
26. Procédé non supercritique de formation d'un aérogel nanoporeux, comprenant les étapes consistant :
 - à former un sol précurseur d'aérogel tel que défini dans l'une quelconque des revendications 1 à 25, ledit sol étant dispersé dans l dit premier solvant et un deuxième solvant,
 - à évaporer presque la totalité dudit deuxième solvant en empêchant une évaporation importante dudit premier solvant, et à permettre au sol de former un gel, le gel comprenant un solide poreux et un fluide dans les pores ;
 - à continuer à empêcher une évaporation importante dudit premier solvant à partir dudit sol jusqu'à une étape

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47. Procédé selon la revendication 29, dans lequel la température du gel au cours du vieillissement est supérieure à 80 °C.
- 5 48. Procédé selon la revendication 29, dans lequel la température du gel au cours du vieillissement est supérieure à 130 °C.
49. Procédé selon la revendication 36, dans lequel le solide poreux a un taux de réduction de volume permanent inférieur à 5 % au cours du retrait du fluide des pores.
- 10 50. Procédé selon la revendication 36, dans lequel le solide poreux a un taux de réduction de volume permanent inférieur à 2 % au cours du retrait du fluide des pores.
51. Procédé selon la revendication 36, dans lequel le solide poreux a un taux de réduction de volume permanent inférieur à 1 % au cours du retrait du fluide des pores.
- 15 52. Procédé selon la revendication 36, dans lequel l'étape de formation de gel est effectuée dans une atmosphère de gélification dans laquelle la concentration de la vapeur du premier solvant dans l'atmosphère de gélification n'est pas activement ajustée.
- 20 53. Procédé selon la revendication 36, dans lequel l'étape de formation de gel est effectuée dans une atmosphère de gélification, la concentration de la vapeur du premier solvant dans l'atmosphère de gélification étant à peu près non ajustée.
- 25 54. Procédé selon la revendication 36, dans lequel le réactif est un alcoolate de métal choisi parmi le tétraéthoxysilane, le tétraméthoxysilane, le méthyltriéthoxysilane, le 1,2-bis(triméthoxysilyl)-éthane et leurs associations.
55. Procédé selon la revendication 36, dans lequel le réactif est le tétraéthoxysilane.
56. Procédé selon la revendication 36, dans lequel l'aérogel poreux et sec, a une porosité supérieure à 60 %.
- 30 57. Procédé selon la revendication 56, dans lequel la porosité est de 60 % à 90 %.
58. Procédé selon la revendication 56, dans lequel la porosité est supérieure à 80 %.
- 35 59. Procédé selon la revendication 36, comprenant en outre l'étape de remplacement d'au moins une partie du fluide dans les pores par un liquide avant l'étape de retrait du fluide des pores.
60. Procédé selon la revendication 59, dans lequel le liquide comprend de l'hexanol.
- 40 61. Procédé selon la revendication 36, comprenant en outre l'étape de recuit de l'aérogel poreux et sec.
62. Procédé selon la revendication 36, dans lequel la pression de l'atmosphère de séchage est inférieure à 3 MPa.
- 45
- 50
- 55

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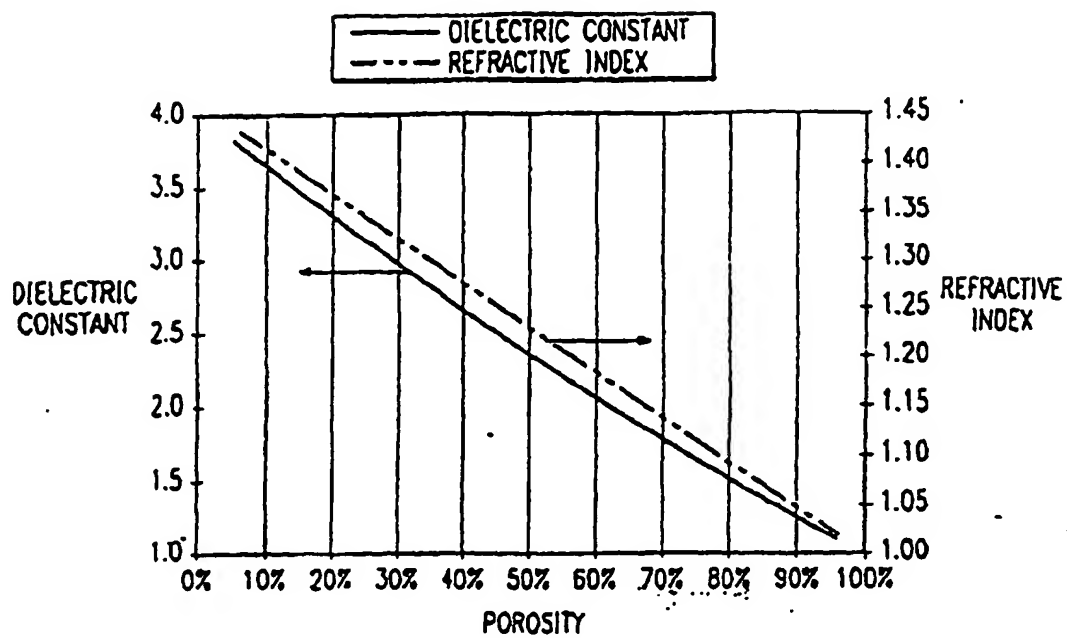


FIG. 3

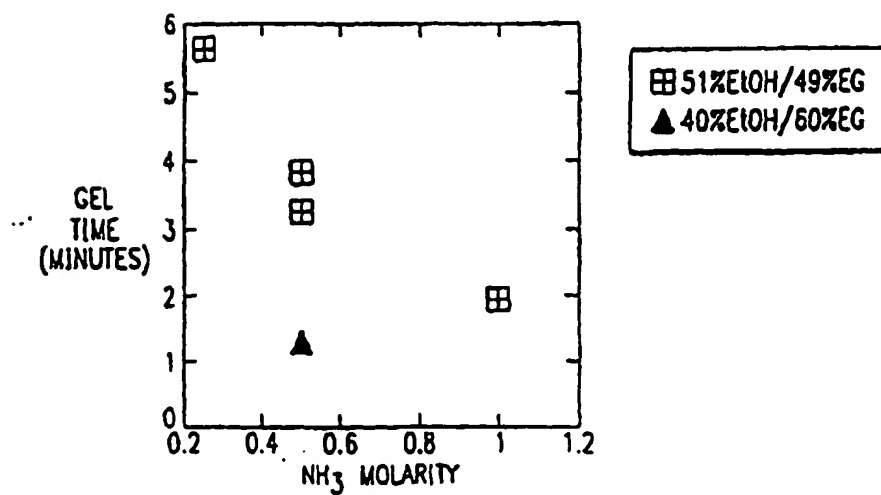


FIG. 4

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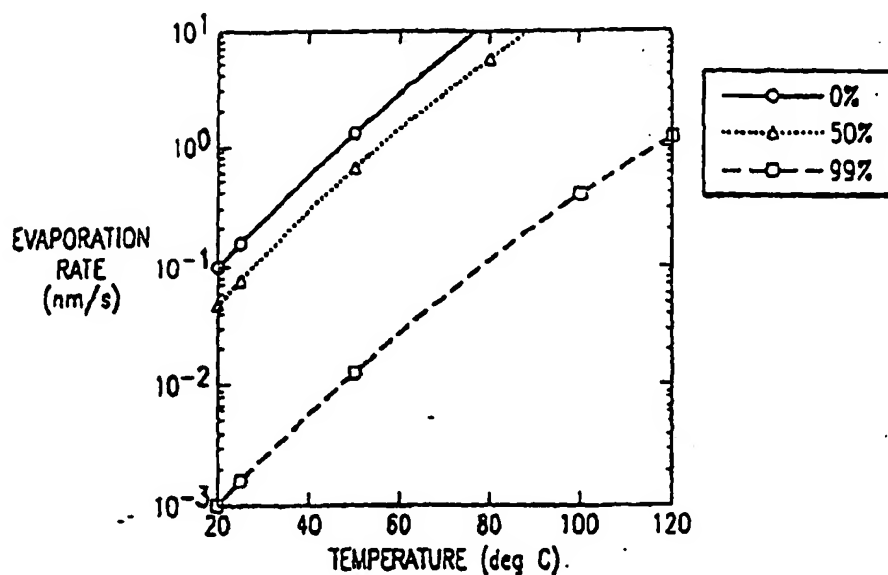


FIG. 7

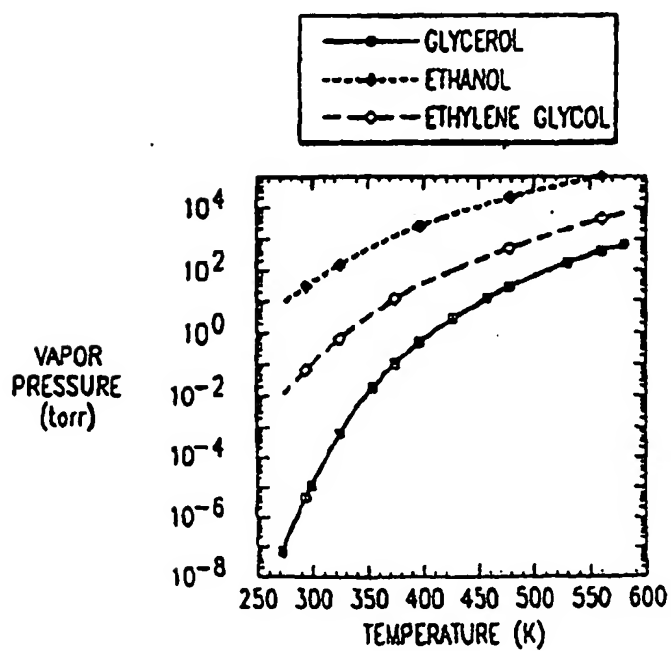


FIG. 8

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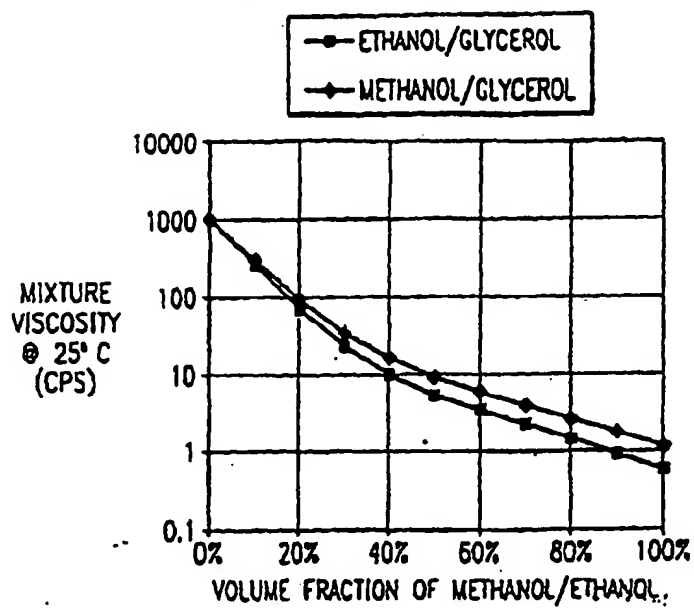


FIG. 11A

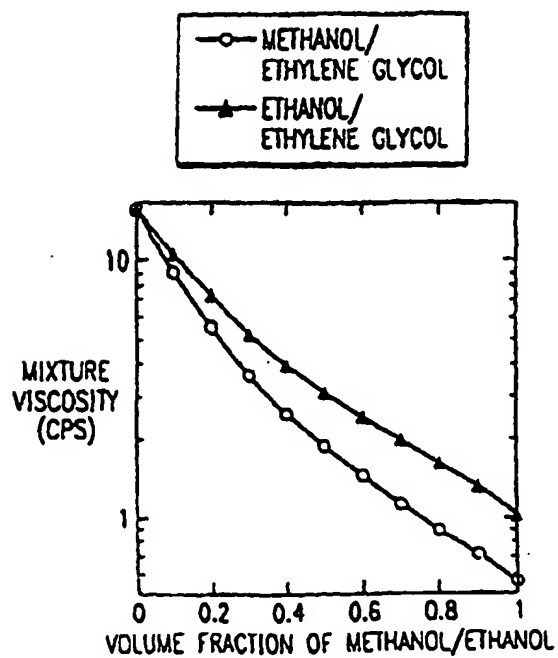


FIG. 11B

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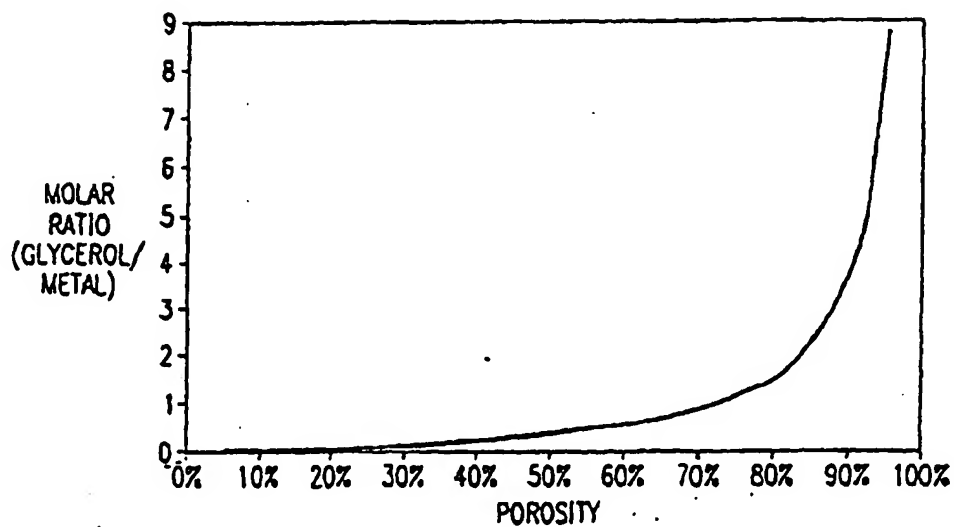


FIG. 14

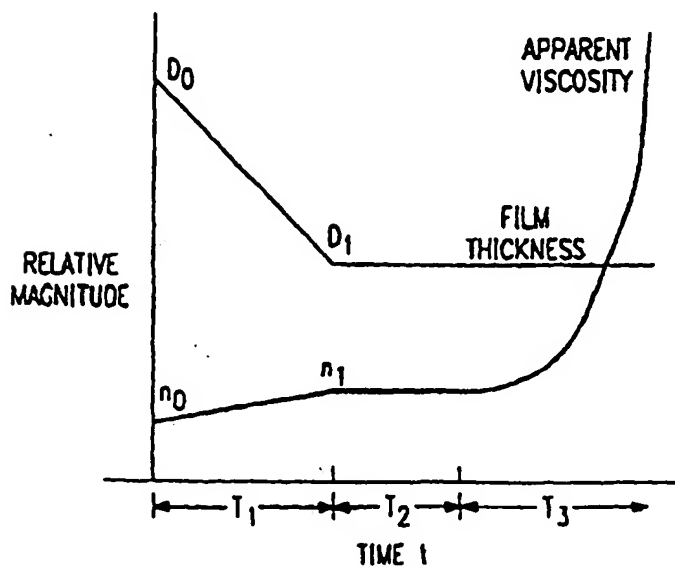


FIG. 15

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